Effects of Added Salts on the Kinetics of Aquation of Tris(5-nitro-1,10-phenanthroline)iron(II)

By **Michael J. Blandamer,*** **John Burgess,** and **Stephen H. Morris,** Department of Chemistry, The University, Leicester LE1 7RH

The rate of aquation of tris(5-nitro-1,10-phenanthroline)iron(II) is increased when tetra-n-butylammonium bromide is added but decreased when potassium bromide, tetraethylammonium bromide, tetramethylammonium bromide, or caesium bromide are added. These effects are analysed in terms of salt effects on both the initial and transition states. In this analysis, use is made of the dependence of the solubility of the ligand, 5-nitro-1,10-phenanthroline, in water on added salt and of parameters which describe cation–cation interactions in mixed-salt solutions.

THE first-order rate constant for aquation of tris(5-nitro-1,10-phenanthroline)iron(II) depends on solvent and varies as both mole fraction and organic co-solvent in an aqueous mixture are changed.[1-4] These observations prompted an examination of the effects of added salts on rate constants for aquation of the complex in water. Interpretation of the effects of added salts on kinetics of reactions in water attracts continued interest.[5] The basis of many treatments for rates of reactions between ions is the Brønsted–Bjerrum equation incorporating suitable theoretical expressions (*e.g.* the Debye–Hückel limiting law) for activity coefficients of the initial and transition states. However, the effects of added 'inert' salts on simple first-order reactions have not been extensively studied. Clarke *et al.* measured the effects of a limited range of salts on the hydrolysis of t-butyl chloride,[6] and more recently some interesting salt effects have been observed in a

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[1] J. Burgess, *Chem. Comm.*, 1967, 1134.
[2] J. Burgess, *J. Chem. Soc.* (*A*), 1968, 1085.
[3] J. Burgess, *J. Chem. Soc.* (*A*), 1969, 1899.
[4] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2351.
[5] B. Perlmutter-Hayman, *Progr. Reaction Kinetics*, 1971, **6**, 239.
[6] G. A. Clarke, T. R. Williams, and R. W. Taft, *J. Amer. Chem. Soc.*, 1962, **84**, 2292.

general base-catalysed solvolysis of two (arylsulphonyl)-methyl perchlorates ($RSO_2CH_2OClO_3$).[7a] Some years ago it was reported that the presence of alkali-metal salts gave rise to small variations in the rate of aquation of the $[Fe(phen)_3]^{2+}$ cation (phen = 1,10-phenanthroline), ascribed to a general ionic background effect,[7b] and that the presence of n-octadecyltrimethylammonium chloride or related salts had ' little or no effect ' on the kinetics of aquation of this complex.[7c] The work reported here was undertaken in the expectation that salt effects on kinetics of reactions in water should be considered in the light of effects of added salts on the ' water structure ' (refs. 8—10) in addition to the more classical ionic-strength effects.[5]

EXPERIMENTAL

Tris(5-nitro-1,10-phenanthroline)iron(II) was prepared in solution by adding a stoicheiometric amount of ligand ($5-NO_2phen$) to a freshly prepared aqueous solution of ammonium iron(II) sulphate. In all cases, alkali-metal and tetra-alkylammonium salts were of the best quality grade. All solutions were prepared using freshly distilled water.

Rate measurements were made on solutions containing 2×10^{-4} mol dm^{-3} of the complex, 10^{-2} mol dm^{-3} of hydrochloric acid, and a weighed amount of salt. New solutions were prepared for each kinetic run.

Kinetic Measurements.—The aquation reaction was followed by measuring the decrease with time of the absorption at 510 nm using a Unicam SP 1800A spectrophotometer. Solutions were contained in 10 mm stoppered silica cells and the absorption recorded at either 1 or 10 s intervals, depending on the half-life of the reaction. Absorption data were logged for at least three half-lives using a Solartron recorder drive unit (A 295) and digital voltmeter (A 220) which was linked to a Facit punch. The paper-tape output obtained recorded absorption data at controlled time intervals together with various control numbers for computer analysis (see below). Spectrophotometer cells were mounted in a thermostatted cell housing which was constructed by winding a heating element and resistance thermometer around a Unicam SP 874 cell housing. The resistance thermometer was one arm of a Wheatstone bridge circuit; the off-balance signal was amplified and fed to a phase-sensitive detector which controlled the current to the electrical heater. In this way, proportional temperature control was achieved yielding a temperature stability of better than ±0·01 K.

Analysis of rate constants. Data on punched tape were analysed (ICL 4130 computer) using the method given by Moore.[11] An ALGOL program was written which incorporated this method as the main procedure after the information had been assembled for analysis.[5] Rate constants for each system were measured at least three times and found to be reproducible to within 2%.

Analysis of the dependence of rate constant on temperature. For a given salt solution, thermodynamic activation parameters $\Delta H^\ddagger$ (enthalpy of activation), $\Delta G^\ddagger$ (Gibbs free energy of activation), and $\Delta S^\ddagger$ (entropy of activation) were calculated using a method based on the Clarke–Glew analysis[12] of the temperature dependence of equilibrium constants. The dependence of rate constant on temperature was fitted to the reference temperature,[12] 310·5 K.

Solubility Measurements.—Solubilities of the ligand, $5-NO_2phen$, were measured by equilibrating at 308 K excess of solid with a given salt solution for >24 h. The ratio of the solubilities in salt solution and water was calculated from relative intensities of absorption at 263 nm. These absorbances were measured for solutions prepared by diluting the equilibrated solutions. In this way, possible complications arising from a dependence of the absorption coefficient on salt concentration were minimised.

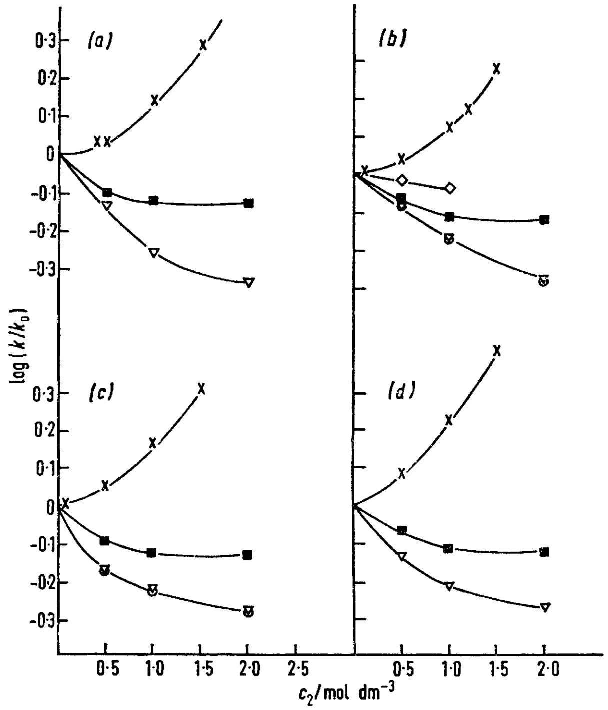

FIGURE 1 Dependence of k/k_0 for the aquation of tris(5-nitro-1,10-phenanthroline)iron(II) on concentration of added salt, c_2: (×), tetra-n-butylammonium bromide; (◇), tetraethylammonium bromide; (■), tetramethylammonium bromide; (▽), potassium bromide; and (○), caesium bromide at 298 (*a*), 308 (*b*), 318 (*c*), and 323 K (*d*)

RESULTS

The aquation of the iron complex was confirmed in all cases as first order and the rate constant in water at 308 K was in good agreement with previously reported values.[13] The aquation was zero order with respect to hydrogen ion in water and the salt solutions over the range $0 \leqslant c_2 < 2$ mol dm^{-3}, where c_2 is the concentration of added salt. In all systems, aquation proceeded to completion.

At a given temperature, the rate of aquation increased when tetra-n-butylammonium bromide was added but decreased when tetramethylammonium bromide was added,

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[7] (*a*) L. Menninga and J. B. F. N. Engberts, *J. Phys. Chem.*, 1973, **77**, 1271; (*b*) J. E. Dickens, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1957, **79**, 1286; (*c*) A. Jensen, F. Basolo, and H. M. Neumann, *ibid.*, 1958, **80**, 2354.

[8] M. J. Blandamer, *Quart. Rev.*, 1970, **24**, 169.

[9] T. S. Sarma and J. C. Ahluwalia, *Chem. Soc. Rev.*, 1973, **2**, 203.

[10] ' Water, A Comprehensive Treatise,' ed. F. Franks, Plenum Press, London, 1973, vol. 3.

[11] P. Moore, *J.C.S. Faraday I*, 1972, **68**, 1890.

[12] E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.

[13] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5752.

although not so dramatically as when potassium bromide was added (Figure 1). A similar pattern was observed at four different temperatures. The effects of other salts were studied at 308 K. Thus, the effect of added caesium bromide was found to be similar to that observed when potassium bromide was added. When tetraethylammonium bromide was added, the rate of aquation decreased slowly, but not so markedly as when tetramethylammonium bromide was added (Figure 1). The change in rate constant with increase in c_2 was, in all cases, insufficient to alter drastically the activation parameters (Table 1).

TABLE 1

Thermodynamic activation parameters at 308 K for aquation of tris(5-nitro-1,10-phenanthroline)iron(II) in aqueous salt solutions

Salt	Concentration, c_2/ mol dm^{-3}	$\Delta G^{\ddagger}$/ kJ mol^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$T\Delta S^{\ddagger}$/ kJ mol^{-1}
	0	90·4	110·5 ± 1·7	19·4
KBr	0·5	91·2	108·8 ± 0·3	17·0
	1·0	91·5	107·2 ± 3·4	15·1
	2·0	92·1	113·1 ± 3·4	20·2
Me_4NBr	0·5	90·9	112·0 ± 0·9	20·4
	1·0	91·1	110·5 ± 1·7	18·7
	2·0	91·2	110·9 ± 2·0	19·1
Bu_4NBr	0·5	90·1	113·7 ± 2·0	22·8
	1·0	89·5	116·6 ± 4·0	26·2
	1·5	88·6	117·2 ± 4	27·6

There was some indication that $\Delta H^{\ddagger}$ increased when salt was added, the change being more obvious for solutions containing tetra-n-butylammonium bromide.

The solubility of the ligand in water increased when tetra-n-butylammonium bromide was added, but this effect was less dramatic when either potassium or tetramethylammonium bromides were added (Table 2). The changes in Gibbs function, $\Delta G^{\ominus}$, for the transfer from a solution of standard state in water to the corresponding standard state in the salt solutions are summarised in Table 2. These transfer functions were calculated assuming that the ligand forms an ideal solution in both water and salt solution. Deviations from ideality are unlikely to account for the observed behaviour.

TABLE 2

Transfer functions, $\Delta G^{\ominus}$, for the ligand 5-nitro-1,10-phenanthroline from a solution where $c_2 = 0$ to one containing added salt at 308 K

Salt	c_2/ mol dm^{-3}	$\Delta G^{\ominus}$/ kJ mol^{-1}	S/S_0 [a]
KBr	0·5	−0·2	0·91
	1·0	0·006	1·02
	2	0·3	1·12
Bu_4NBr	1	7·6	19·5
	1·5	8·8	31·2
Me_4NBr	0·5	0·7	1·31
	1	0·7	1·33

[a] Solubility of ligand in salt solution to that in water.

Analysis of Salt Effects.—Irrespective of the detailed mechanism of aquation, the reaction involves a dipositive iron complex, M_i^{2+}, in the initial state and a dipositive iron complex, M_t^{2+}, in the transition state [equation (1)].

$$M_i^{2+} \longrightarrow (M_t^{2+})^{\ddagger} \longrightarrow \text{products} \qquad (1)$$

Equation (1), taken in conjunction with a measured first-order rate constant, can include both mechanistic possibilities; *i.e.* that the reaction is either dissociative or involves attack by water at the iron atom. In terms of the Brønsted–Bjerrum theory, the rate constant k in a salt solution is given by equation (2), where γ_i and γ_t

$$\log (k/k_0) = \log (\gamma_i/\gamma_t) \qquad (2)$$

are the activity coefficients of the initial and transition states and k_0 is the rate constant when $c_2 = 0$. Equation (2) is a rare example where the observable, k/k_0, is equal to the ratio of two single ion activity coefficients.

Because the ratio, k/k_0, depends on salt concentration, γ_i and γ_t must differ in respect of their dependence on salt concentration. For example, the Debye–Hückel limiting law [equation (3); z_i is the valency of the ion, I (the ionic strength [14]) $= \frac{1}{2}\sum_i c_i z_i^2$, and S is a known function [14] of temperature and solvent permittivity] cannot account for the observations reported here. Consequently,

$$\log \gamma_i = -S z_i^2 I^{\frac{1}{2}} \qquad (3)$$

more complicated equations are required to express the dependence of γ_i on I. A number of equations were tested but each involved new and unknown quantities. Two examples illustrate the essential features of this analysis.

The Debye–Hückel equation relates γ_i and I as shown in equation (4), where B is a known function of temperature

$$\log \gamma_i = -S z_i^2 I^{\frac{1}{2}}/(1 + B a_i I^{\frac{1}{2}}) \qquad (4)$$

and solvent permittivity [14] and a_i is the distance of closest approach for the i ion. Thus a_i is determined by both the i ion and other ions in solution. As a_i increases, $\log \gamma_i$ becomes less negative than predicted by the limiting law [equation (3)]. In calculating the ionic strength, only the concentrations of added salts were important, the concentrations of complex and acid being, by comparison, negligibly small. Combination of equations (2) and (4) produces two a values, a_i for the initial state and a_t for the transition state. Consequently, if $a_t > a_i$ the transition state will be destabilised by added salt to a greater extent than the initial state [relative to that required by the limiting law, equation (3)] and so the rate constant will decrease. Alternatively, if $a_i > a_t$ the rate constant will increase. The resulting expression was recast in a form from which a_t could be calculated by a least-squares fitting program (BASIC for PDP-10 computer) for specified values of a_i. The best fit was judged to be obtained when the standard deviation between observed and calculated values of k/k_0 was a minimum. This minimum was sought using a process of trial and error. Typical values of a_i and a_t are summarised in Table 3 and a comparison between observed and predicted values of k/k_0 is shown in Figure 2.

TABLE 3

Parameters obtained from analysis of dependence of $\log(k/k_0)$ on c_2 at 308 K

Salt	a_i/Å	a_t/Å	ΔB/ mol^{-1} dm^3
KBr	5·2	11	−0·142
Me_4NBr	4·9	6·6	−0·066
Bu_4NBr	5·3	2·9	+0·181

In analysis of salt effects in kinetics, Guggenheim's [15] modification of the Guntelberg [16] equation has attracted

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[14] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1965, 2nd edn., revised.

[15] E. Guggenheim, *Phil. Mag.*, 1935, **19**, 588.

[16] E. Guntelberg, *Z. phys. Chem.*, 1926, **123**, 199.

attention.[17] For a single ion, the activity coefficient γ_i is related to the ionic strength by equation (5). Here

$$\log \gamma_i = -[S z_i^2 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})] + B_i I \qquad (5)$$

B_i is an ionic-interaction coefficient which takes account of specific ion–ion and ion–solvent interactions. With increase in B_i, log γ_i increases and the i ion is destabilised.

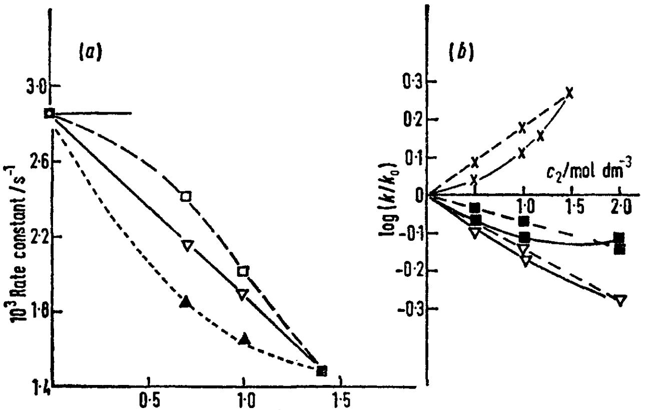

FIGURE 2 Comparison of observed and predicted dependences of k/k_0 on concentration of added salt for the aquation of the ion $[Fe(5\text{-}NO_2phen)_3]^{2+}$ at 308 K: (*a*) effect of added potassium bromide, observed (▽), predicted using equations (4) (▲) and (6) (□); (*b*) effect of added salts, observed (——), and predicted dependence (- - - -) according to equation (6). (Parameters for the equations are summarised in Table 3.) See caption to Figure 1 for key to symbols in (*b*)

Combination of equations (2) and (5) produces two B_i values, $B_{\rm i}$ for the initial state and $B_{\rm t}$ for the transition state. Because the first term on the right-hand side of equation (5) is the same for both initial and transition states, the final equation for k/k_0 has the simple form (6), where $\Delta B = B_{\rm i} - B_{\rm t}$. Thus, if ΔB is positive the initial state is

$$\log(k/k_0) = \Delta B \,.\, I \qquad (6)$$

destabilised more than the transition state by added salt and so the rate constant increases. If ΔB is negative the rate constant decreases. The kinetic data for each system was fitted to equation (6) to obtain best-fitting values for ΔB (Table 3). A comparison between observed and calculated values of k/k_0 is shown in Figure 2.

DISCUSSION

The significant result is that the rate of an aquation reaction can either decrease or increase depending on the nature of the 1 : 1 salt added. Moreover, the rate of aquation of a cation is found to be sensitive to the cation of the added salt. The importance of cation–cation interactions, especially in the context of mixed aqueous-salt solutions, is, of course, well known (*cf.* Young's rule [18,19]).

Although the activation enthalpy, $\Delta H^{\ddagger}$, shows only a small change when salt is added, the change is of a similar order of magnitude to that observed when, say, an alcohol is added to t-butyl chloride in water [20–23] when judged in terms of the mole fraction of either added salts or added co-solvent. For example, in the hydrolysis of t-butyl chloride, $\Delta H^{\ddagger}$ has a minimum when the mole fraction, x_2, of t-butyl alcohol is *ca.* 0·05, the value of $\Delta H^{\ddagger}$ being 18·8 kJ mol^{-1} (19%) below that of $\Delta H^{\ddagger}$ in water.[21] Similarly in the reaction between Ni^{2+} ions and 2,2′-bipyridyl (bipy) in water–t-butyl alcohol mixtures [23] a minimum in $\Delta H^{\ddagger}$ occurs near $x_2 = 0{\cdot}04$, which is 6·3 kJ mol^{-1} (13%) below $\Delta H^{\ddagger}$ for reaction in water, whereas $\Delta G^{\ddagger}$ changes by only 2·1 kJ mol^{-1}. Similar but less-striking effects were observed for the latter reaction in ethanol–water.[23,24]

In the aquation of the present iron complex (Table 1) in solutions containing the highest concentration of tetra-n-butylammonium bromide, $\Delta H^{\ddagger}$ is *ca.* 7·5 kJ mol^{-1} (7%) below that for reaction when $c_2 = 0$, although the change in $\Delta G^{\ddagger}$ is much smaller, *ca.* 2·1 kJ mol^{-1}. Clearly the salt effects observed here are comparable to solvent effects and, moreover, the relative sensitivities of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are similar. In both cases, added solvent and added salt, $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ change in such a way as to minimise the effect on $\Delta G^{\ddagger}$. However, these compensation effects are subject to considerable controversy [25–28] at the present time so this point will not be taken further. Nevertheless, detailed interpretation of changes in $\Delta H^{\ddagger}$ following addition of a salt requires information concerning partial enthalpies of the initial and transition states. Unfortunately, this information is not available. Therefore in this paper the analysis is confined to those factors which control $\Delta G^{\ddagger}$. In general, interpretation of such trends is more straightforward.

Analysis of the kinetic data using classical expressions for the activity coefficients, $\gamma_{\rm i}$ and $\gamma_{\rm t}$, proved disappointing. While the derived expressions can account for the broad patterns observed, agreement between theory and experiment is obviously poor (Figure 2). The a values (Table 3) obtained are reasonable, but values of ΔB are somewhat larger than expected when compared with B values for salts in water.[17] However, these quantities, taken alone, probably do little to advance the understanding of the kinetic data (see below).

The kinetic salt effects do, however, follow a clear-cut pattern in respect of the postulated effects of these salts and ions on water–water interactions. Thus, in terms of their water structure-breaking action, the order is [8,9,29] $K^+ > Me_4N^+ > Et_4N^+ > Bu_4N^+$, the

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[17] J. E. Prue, A. J. Read, and G. Romeo in ' Hydrogen-bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, p. 155.

[18] T. F. Young, Y. C. Wu, and A. A. Krawetz, *Discuss. Faraday Soc.*, 1957, **24**, 27, 77, 80.

[19] H. L. Anderson and R. H. Wood, ref. 10, ch. 2.

[20] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[21] R. E. Robertson and S. E. Sugamori, *J. Amer. Chem. Soc.*, 1969, **91**, 7254.

[22] J. B. Hyne, ref. 17, p. 99.

[23] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1973, **12**, 113.

[24] See H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2207.

[25] D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.

[26] R. Lumry and S. Rajendar, *Biopolymers*, 1970, **9**, 1125.

[27] O. Exner, *Nature*, 1964, **201**, 488.

[28] O. Exner and V. Beranek, *Coll. Czech. Chem. Comm.*, 1973, **38**, 781.

[29] R. L. Kay, ref. 10, ch. 4.

latter ion being classed as a structure former. The tetraethylammonium ion is thought to be close to the borderline between structure-forming and structure-breaking classes,[29] and here the effect on the rate constant was found to be small (Figure 1). However, this simple approach is insufficient because these terms, structure making and breaking, refer to the effects of these ions on water in their solution standard states, *i.e.* in the absence of ion–ion interactions. In analysis of the kinetic data, interactions in real solutions must be examined, consideration being given to the effects of overlapping solvent co-spheres between the ions.[30–32] In an attempt to probe the relation between k/k_0 and the properties of these salt solutions, we plotted k/k_0 against both G^E and ϕ, where G^E is the excess molar Gibbs function for the salt solution [33,34] (calculated from the mean ionic activity coefficient for the salt) and ϕ is the practical osmotic coefficient of the solvent (KBr data from ref. 14 and tetra-alkylammonium data from ref. 35). However, no obvious pattern emerged (Figure 3). This is not altogether surprising because k/k_0 depends on salt effects which operate on both initial and transition states. Some method of estimating these separate contributions is required but this presupposes detailed knowledge of the mechanism of aquation.

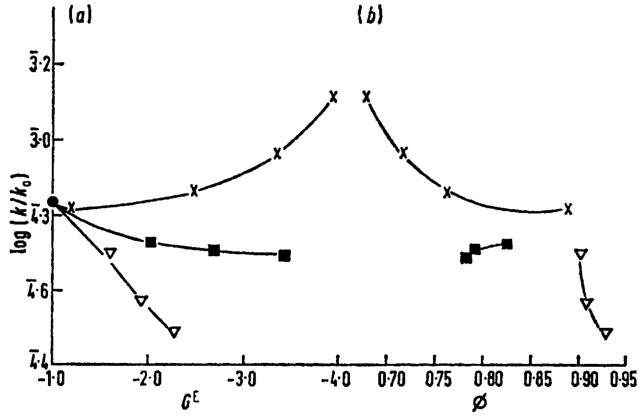

FIGURE 3 Dependence of k/k_0 at 298 K on (*a*) G^E (kJ mol^{-1}) for the salt solutions and (*b*) osmotic coefficient, ϕ, for the solvent in the salt solutions; for key see caption to Figure 1

Substitution reactions of octahedral transition-metal complexes, particularly low-spin d^6 species, are generally dissociative in character. The mechanism of aquation of complexes of the type $[Fe(phen)_3]^{2+}$ has not been unequivocally established. Substitution reactions of closely related low-spin iron(II) complexes, $[Fe(CN)_5L]^{n+}$, are dissociative in mechanism with several recent demonstrations of a limiting S_N1 (or *D*) mechanism, as for example when L = PhNO,[36] NO,[37] or pyridine (py).[38,39] The kinetic pattern for aquation of the ion $[Fe(bipy)_3]^{2+}$ is consistent with a five-co-ordinate intermediate containing one monoprotonated unidentate bipy ligand.[40,41] On the other hand, an associative mechanism has been proposed for one path in the reaction of $[Fe(phen)_3]^{2+}$ and related complexes with hydroxide [42,43] or cyanide ion.[42,44] The relative nucleophilicity of water for Fe^{II} as compared with cyanide or hydroxide ion is very small, so associative attack of water at iron(II) seems relatively improbable. However, the geometry of cations of the $[Fe(phen)_3]^{2+}$ type is such that it is possible for water molecules to be present in the voids between the planar phen ligands [7c] and are thus favourably situated for interaction with the iron(II) centre. From the available evidence, the most probable mechanism for aquation of the ion $[Fe(5\text{-}NO_2phen)_3]^{2+}$ is dissociative, though some small degree of associative character cannot be ruled out. Therefore, in the following discussion we concentrate on the probable effects and consequences of the addition of salts on a dissociative mode of aquation for this complex.*

In the aquation an Fe–N bond is stretched or broken on going from the initial to the transition state. While the NO_2 group of the 5-NO_2phen ligand is hydrogen bonded to the solvent,[45] more of the hydrophobic phen ring is exposed to the water. In these terms, the transition state is more hydrophobic than the initial state. The increase in a ($a_t > a_i$) for potassium bromide and tetramethylammonium bromide solutions is consistent with this expansion on going to the transition state. The decrease in a ($a_i > a_t$) for tetra-n-butylammonium bromide sets this particular system apart. Here, apparently, the effective volume of the transition state is less than that of the initial state. It is to be noted, however, that tetra-alkylammonium salts form hydrate clathrates [8,9,45–47] in which the alkyl groups occupy voids in the structure formed by hydrogen-bonded water molecules. Analysis of the properties

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* Preliminary results on the variation of the aquation rate of the ion $[Fe(5\text{-}NO_2phen)_3]^{2+}$ with pressure suggest a large positive activation volume for this reaction, which is consistent with a dissociative mechanism (J. Burgess, J. M. Lucie, and D. R. Stranks, unpublished work).

[30] H. L. Friedman and C. V. Krishnan, ref. 10, ch. 1.

[31] R. W. Gurney, ' Ionic Processes in Solution,' McGraw-Hill, New York, 1953.

[32] J. F. Desnoyers, M. Arel, G. Perron, and C. Jolicoeur, *J. Phys. Chem.*, 1969, **73**, 3346.

[33] H. L. Friedman, *J. Chem. Phys.*, 1960, **32**, 1351.

[34] Y-C. Wu and H. L. Friedman, *J. Phys. Chem.*, 1966, **70**, 166.

[35] S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, 1964, **68**, 911.

[36] D. Pavlovic, I. Murati, and S. Asperger, *J.C.S. Dalton*, 1973, 602.

[37] L. Dozsa, I. Szilassy, and M. T. Beck, *Magyar Kém. Folyóirat*, 1973, **79**, 45.

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[39] B. Jezowska-Trzebiatowska, A. Keller, and J. Ziolkowski, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1972, **20**, 449.

[40] See, for example, F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, 2nd edn., pp. 218—219.

[41] R. Davies, M. Green, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1172.

[42] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706.

[43] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

[44] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

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[46] G. A. Jeffrey and R. K. McMullan, *Progr. Inorg. Chem.*, 1967, **8**, 43.

[47] D. W. Davidson, ref. 10, vol. I, ch. 3.

of the corresponding salt solutions have often envisaged a similar arrangement. In these terms, it is suggested that the dissociating ligand is accommodated within comparable voids present in this tetra-alkylammonium salt solutions system and so the effective volume of the substrate falls on going to the transition state. The trend in ΔB can also be interpreted in the same way. This idea is partially substantiated by solubility data for the ligand. Thus, when the ligand is completely removed, the data show a salting-in action by tetra-n-butylammonium bromide which is considerably larger than that exerted by either potassium bromide or tetramethylammonium bromide. Salting in of a hydrophobic solute[48] by tetra-n-butylammonium bromide has been reported in numerous cases,[49] that where the solute is benzene being particularly well established.[50,51] Therefore, we suggest that the change in chemical potential of the transition state is dominated by the effects of increased exposure to water of the more hydrophobic ligand. The actual effect on the transition state will be less dramatic than that calculated for the ligand alone.

Investigations into medium effects on solubilities of the salts of complex ions is in progress.[52] Unfortunately, application of this information to analysis of the kinetic data is not straightforward because solubility is a function of both cation and anion. Some preliminary studies[53] have shown, however, that the solubility of the perchlorate salt of this iron complex increases rapidly when tetra-n-butylammonium bromide is added but only slowly when potassium bromide is added. [The Debye–Hückel limiting law, equation (3), predicts that solubility should increase when an 'inert' salt is added.] However, $-\Delta G^{\ominus}$ for transfer of the complex salt from water to a 1·0 mol dm^{-3} solution of tetra-n-butylammonium bromide is less than that for the ligand. In contrast, for transfer of the salt from water to a 1·0 mol dm^{-3} solution of potassium bromide, $-\Delta G^{\ominus}$ is more than that for the transfer of the ligand. If similar conclusions can be drawn for the single-ion initial states, then the increase in rate constant (or decrease in $\Delta G^{\ddagger}$) follows from a more dramatic stabilisation of the transition state when tetra-n-butylammonium bromide is added. In contrast, when potassium bromide is added, the initial state is stabilised to a greater extent than the transition state (Figure 4).

These conclusions are attractive but rely on a possibly unrealistic extrapolation from solubility data. An alternative approach uses thermodynamic data for salt solutions. It is noteworthy that the pattern shown by the rate constant agrees with that drawn from an examination of Friedman's g_0 functions.[19] The latter quantities are obtained from analysis of the thermodynamics of mixing of salt solutions at fixed ionic strength. Furthermore, these parameters can be used to probe interactions between like-charged ions. In the present analysis we used values of g_0 (actually RTg_0) obtained for solutions at unit ionic strength and estimated the effects of added cation on both initial and transition states. The published g_0 values[19] show that RTg_0 tends to be positive for mixtures of salts where one cation is hydrophilic[32] and the other hydrophobic (*e.g.* caesium bromide + tetra-n-propylammonium bromide) and to be negative and smaller in magnitude for mixtures of salts where both cations are either hydrophilic (*e.g.* sodium bromide + potassium bromide) or hydrophobic (*e.g.* tetraethylammonium bromide + tetra-n-propylammonium bromide). Consequently, we conclude that addition of a hydrophobic cation (*e.g.* tetra-n-butylammonium) to a solution of the iron complex destabilises the initial state to a greater extent than the hydrophobic transition state is stabilised and so the rate constant increases. In contrast, addition of an alkali-metal cation (*e.g.* potassium) will destabilise the hydrophobic transition state to a greater extent than the initial state is stabilised and so the rate constant will decrease (Figure 4). While the outcome of both analyses is satisfactory, different conclusions are reached concerning the effects of the salts on the two states. At this stage we see no obvious way of distinguishing between the two possibilities summarised in Figure 4.

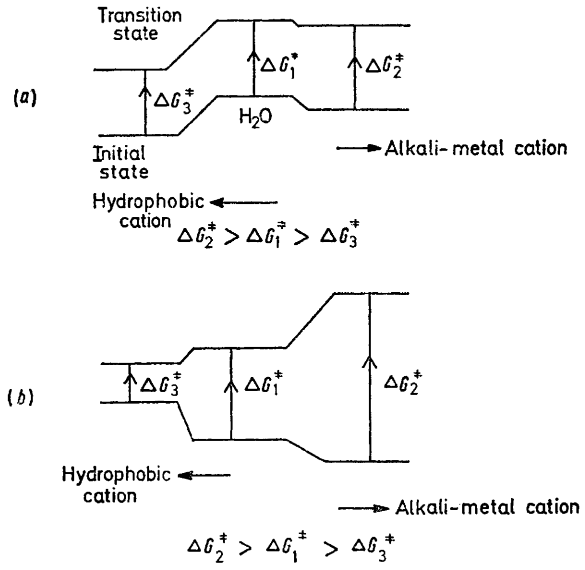

FIGURE 4 Summary of conclusions reached concerning effects of added salts on the initial and transition states in the aquation of the ion $[\mathrm{Fe}(5\text{-}\mathrm{NO}_2\mathrm{phen})_3]^{2+}$; inferred from (*a*) solubility data and (*b*) g_0 functions

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